Estimation of Rate Constants for Gas-Phase Reactions of Chrysene, Benz[a]anthracene, and Benzanthrone with OH and NO Radicals via a Relative Rate Method in CCl Liquid Phase-System

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Estimation of rate constants for gas-phase reactions of chrysene, benz[*a*]anthracene, and benzanthrone with OH and NO_3 radicals via a relative rate method in CCl_4 liquid phase-system

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Abstract

CCl_4 liquid-phase reaction kinetics of polycyclic aromatic compounds (PACs), including chrysene (CHRY), benz[*a*]anthracene (BaA), and benzanthrone (BA), with NO_3 radicals were investigated at 273 K using a relative rate method with naphthalene (NA) as the reference compound. The obtained relative reaction rates of CHRY, BaA, and BA to NA were 1.76 ± 0.08, 2.27 ± 0.20, 0.75 ± 0.01, respectively. CHRY, BaA, and BA are semi-volatile PACs with four aromatic rings. They are chemically modified into mutagenic nitropolycyclic aromatic compounds via gas-phase OH or NO_3 radical-initiated reactions. Based on the PACs relative reactivity in the CCl_4 liquid phase-system, the rate constants at 298 K for the gas-phase reaction of CHRY, BaA, and BA with OH radicals and those of CHRY, BaA, and BA with NO_3 radicals were estimated to be (in $cm^3molecule^{-1}s^{-1}$): CHRY, $(4.4 \pm 0.3) \times 10^{-11}$ and $(9.2 \pm 3.2) \times 10^{-28}$ $[NO_2]$; BaA, $(5.3 \pm 0.5) \times 10^{-11}$ and $(1.3 \pm 0.5) \times 10^{-27}$ $[NO_2]$; BA, $(2.3 \pm 0.1) \times 10^{-11}$ and $(3.1 \pm 1.1) \times 10^{-28}$ $[NO_2]$.

Keywords: PAH, nitro-PAH, radical-initiated reactions, atmospheric nitration

Introduction

Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) are a class of polycyclic aromatic compounds (PACs), most of which exhibit direct-acting mutagenicity or carcinogenicity [1]. They are detected in filtered samples of ambient air [2] or combustion emissions [3], including diesel exhaust particles [4] and airborne particles [5]. For example, atmospheric 1-nitropyrene (1-NP) is produced during combustion [2, 5], whereas, 2-nitrofluoranthene (2-NF) is found in higher concentrations in airborne particles [2, 6], and it is considered a product of atmospheric gas-phase reactions of parent fluoranthene (FLRA) with nitrogen oxides initiated by hydroxyl (OH) radicals or nitrate (NO_3) radicals [7–9]. Benzanthrone (BA) is a less volatile PAC than FLRA, sublimation pressures at 298 K (*P*s(298K)) for BA and FLRA are 2×10^{-5} Pa and 1.23×10^{-3} Pa, respectively [10, 11]. Nevertheless, BA also reacts with OH and NO_3 radicals in the gas phase, resulting in 2-nitrobenzanthrone (2-NBA) [12]. Vapor pressures of chrysene (CHRY) and benz[*a*]anthracene (BaA) are comparable to the vapor pressure of BA, i.e., *P*s(298 K) are 1.2×10^{-6} Pa for CHRY and 2.7×10^{-5} Pa for BaA [10]. Thus, CHRY and BaA may also react with OH and NO_3 radicals in the gas phase, resulting in toxic nitro-PAHs. The rate constants for the reactions of BA, CHRY, and BaA with OH or NO_3 radicals, although poorly understood, are important factors, because they may control their nitro-derivatives' concentrations in the atmosphere.

OH and NO_3 radical-initiated reactions of polycyclic aromatic hydrocarbons (PAHs) were studied extensively [13–18]. However, the rate constants for the gas-phase reactions of semi- and low-volatile PACs (those with four or more aromatic rings) cannot be accurately determined using conventional methods such as large-chamber experiments [8] and fast-flow discharge methods [19], because they are mainly deposited on the walls of the reaction system due to their low vapor pressures. We established a method for determining the rate constants of the gas-phase reactions of low-volatile organics with OH radicals using a relative-rate technique in CCl_4 liquid phase-system [20, 21]. In particular, we obtained several PACs' relative reactivity indices, by reacting them with NO_3 radicals in a CCl_4 liquid phase-system. These indices can be used to predict the reaction rate constants of low-volatile PACs with OH or NO_3 radicals in the gas phase.

In the present study, we estimate the rate constants of the gas-phase reactions of CHRY, BaA, and BA with OH and NO_3 radicals based on their reactivity with other PACs in the CCl_4 liquid phase-system.

Material and methods

Relative-rate method in the N_2O_5–NO_3–NO_2–CCl_4 liquid phase-system

The gas-phase reactions' rate constants of CHRY, BaA, and BA with OH and NO_3 radicals were predicted using the relative-rate method in a N_2O_5–NO_3–NO_2–CCl_4 liquid phase-system [20, 21]. Detailed descriptions of this method were provided in the previous reports [20, 21]. As the source of NO_3 radicals, we used N_2O_5 synthesized by a two-step dehydration of a concentrated HNO_3 aqueous solution with P_2O_5 [22]. The prepared N_2O_5 was dissolved in CCl_4. The N_2O_5–CCl_4 solution was added to a CCl_4 solution of each PAC with stirring. Naphthalene (NA) was used as the reference substrate, because the rate constants of its reactions with OH and NO_3 radicals are well established. The N_2O_5 initial concentration was up to 32 mmol L^{-1}, and the PACs initial concentrations were: 0.5 µmol L^{-1} for FLRA, fluorene (FLRE), 2-methylnaphthalene (2-MNA), NA, phenanthrene (PHE), pyrene (PY), CHRY, BaA, and triphenylene (TP); 1 µmol L^{-1} for BA, acenaphthene (ACE), 1-methylnaphthalene (1-MNA), and 2,3-dimethylnaphthalene (2,3-DMNA); 5 µmol L^{-1} for 1-nitronaphthalene (1-NNA). During the reaction, an aliquot of the reaction solution (normally 1 mL) was sampled at 30-sec intervals, and added to 200 µL acetaldehyde to terminate the radical reaction. The remaining PAC was determined through high-performance liquid chromatograph (HPLC) with either a spectrofluorometric or a UV–vis spectrophotometric detector. The rate constant ratio of each PAC to NA was determined in the N_2O_5–NO_3–NO_2–CCl_4 system using a relative-rate method at 273 ± 1 K. CCl_4 was employed as an aprotic non-polar solvent enabling N_2O_5 to exist as a covalent molecular species to generate NO_3 following equilibrium between molecular N_2O_5, NO_3, and NO_2 ($N_2O_5 \rightleftarrows NO_3 + NO_2$). Assuming that the reaction with NO_3 radicals is the only loss process of the PACs, the natural logarithmic plots of each PAC's concentration against NA at specific reaction times (usually within 150 sec) relative to its initial

concentration provide the rate constant ratio between each PAC and NA, according to the following equations:

NO_3 + PAC → Products (1)

NO_3 + NA → Products (2)

$\ln([PAC]_0/[PAC]_t) = k_1/k_2 \ln([NA]_0/[NA]_t)$ (3)

where $[PAC]_0$ and $[NA]_0$ are the initial concentrations, and $[PAC]_t$ and $[NA]_t$ are the concentrations at reaction time t. The k_1 and k_2 are the rate constants for reactions 1 and 2, respectively.

PACs chemical analysis in the system

The CCl_4 solutions containing each PAC were diluted with methanol at appropriate concentrations. An aliquot of each sample solution was analyzed using a Hitachi L-6200 HPLC-system equipped with either a Hitachi F-1050 spectrofluorometric detector or a Hitach L-4200 UV–vis spectrophotometric detector using an Inertsil ODS-3 column (GL science, 3.0 mm i.d. × 250 mm). The mobile phase of the analysis system was methanol/water (4/1, v/v).

Chemicals

Authentic standards of PACs were obtained from Sigma-Aldrich Co. or Wako Pure Chemical Ind. Ltd. All solvents and other chemicals used were HPLC or analytical grades from Wako Pure Chemical Ind., Ltd.

Results and Discussion

Applying linear regression to the plot of $\ln([PAC]_0/[PAC]_t)$ vs. $\ln([NA]_0/[NA]_t)$, the slope of the regression line is equivalent to the rate constant ratio k_1/k_2. The relative rate plots from the experiments in accordance with Eq (3) are presented in Figs. 1a–1c. Good linear plots with no intercept are obtained, validating the relative rate method as an effective tool to obtain the rate constants ratio for the studied reactions. The k_1/k_2 values for CHRY, BaA, and BA obtained by the least-square analysis and the rate constant ratios for the gas phase OH or NO_3 radical-initiated reactions of PAC to those of NA (k_{PAC}-

$_{OH}/k_{NA-OH}$ and $k_{PAC-NO3}/k_{NA-NO3}$) are given in Table 1. These values were obtained by using previously reported rate constants [13, 14, 17, 18, 23–25]. For the gas-phase NO_3-reaction, the rate constant of the NO_2-dependent reaction was used as $k_{PAC-NO3}$ (see footnote of Table 1).

The k_1/k_2 ratio correlates well with $k_{PAC-NO3}/k_{NA-NO3}$ [i.e., $\log(k_{PAC-NO3}/k_{NA-NO3}) = 1.27*\log(k_1/k_2) + 0.09$, correlation coefficient $r = 0.95$, significance level $p < 0.001$] and k_{PAC-OH}/k_{NA-OH} [i.e., $\log(k_{PAC-OH}/k_{NA-OH}) = 0.78*\log(k_1/k_2) + 0.07$, $r = 0.97$, $p < 0.001$] [21]. Based on these relationships and the rate constant ratio k_1/k_2 for CHR, BaA, and BA (1.76, 2.27, and 0.75, respectively), the ratios of the rate constant for the gas phase NO_3 or OH radical-initiated reactions of these PACs to those of NA ($k_{PAC-NO3}/k_{NA-NO3}$ and k_{PAC-OH}/k_{NA-OH}, respectively) can be predicted. Based on the obtained rate constant ratios $k_{PAC-NO3}/k_{NA-NO3}$ and k_{PAC-OH}/k_{NA-OH} and the known rate constants for the gas phase NO_3 or OH radical-initiated reactions of NA {$k_{NA-NO3} = (3.66 \pm 1.26) \times 10^{-28}[NO_2]$ $cm^3molecule^{-1}s^{-1}$, $k_{NA-OH} = (2.39 \pm 0.10) \times 10^{-11}$ $cm^3molecule^{-1}s^{-1}$} [18, 26], the rate constants at room temperature for the gas-phase reaction of CHRY, BaA, and BA with OH radicals and those of CHRY, BaA, and BA with NO_3 radicals are (in $cm^3molecule^{-1}s^{-1}$): CHRY, $(4.4 \pm 0.3) \times 10^{-11}$ and $(9.2 \pm 3.2) \times 10^{-28}$ $[NO_2]$; BaA, $(5.3 \pm 0.5) \times 10^{-11}$ and $(1.3 \pm 0.5) \times 10^{-27}$ $[NO_2]$; BA, $(2.3 \pm 0.1) \times 10^{-11}$ and $(3.1 \pm 1.1) \times 10^{-28}$ $[NO_2]$. The indicated errors were based on the standard deviations of the k_1/k_2 ratios from three replicate measurements and the uncertainty of the rate constants of the reference compound. The obtained rate constants of the gas-phase OH reaction using this system for CHRY and BaA agreed closely with previously estimated values, 3.4×10^{-11} $cm^3molecule^{-1}s^{-1}$ and 5.3×10^{-11} $cm^3molecule^{-1}s^{-1}$, respectively, using an empirical relationship between k_{PAC-OH} and the Hückel hardness factors [26].

The tropospheric lifetimes of CHRY, BaA, and BA with respect to the gas-phase reaction with OH and NO_3 radicals (Table 2) are calculated by combining the corresponding reaction rate constants with the ambient atmospheric concentrations (in molecule cm^{-3}) of OH and NO_3 radicals applying a 12-h average daytime concentration of 1.9×10^6 [27] and 5×10^8 [23], respectively. Indeed, the OH radical reaction during daytime is the dominant CHRY, BaA, and BA loss process. Thus, considerable atmospheric formation of CHRY, BaA, and BA nitro-derivatives is anticipated from their reaction with

OH radicals. The NO_3 radical reaction is less important by 2–3 orders of magnitude than the OH radical reaction in the atmospheric removal of CHRY, BaA, and BA.

Acknowledgments

This work was supported in part by the Environment Research and Technology Development Fund (5-1306) of the Ministry of the Environment, Japan and the cooperative research program of Institute of Nature and Environmental Technology, Kanazawa University.

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Figure Captions

Figure 1. Plots of Eq (3) for the reaction of NO_3 radicals with CHRY, BaA, and BA in the CCl_4 liquid-phase system.

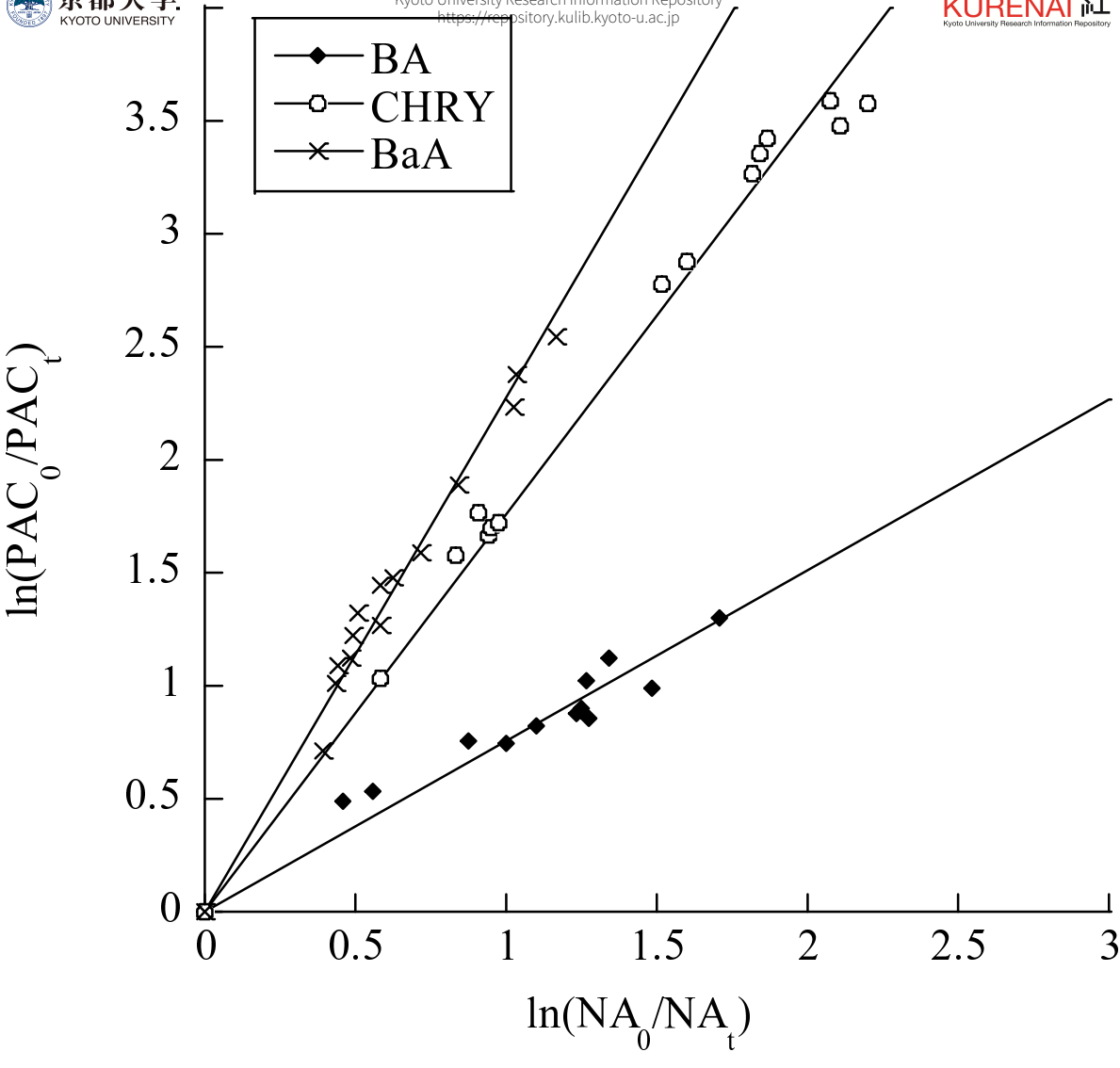

Table 1: Rate constant ratios k_1/k_2 obtained in this study. $k_{PAC\text{-}OH}$ and $k_{PAC\text{-}NO3}$ are rate constants for the gas phase reactions of corresponding PACs with OH radicals and NO_3 radicals, respectively.

Compound	k_1/k_2	$10^{11}k_{PAC\text{-}OH}$[a]	$10^{28}[NO_2]^{-1}k_{PAC\text{-}NO3}$[b]
Chrysene (CHRY)	1.76 ± 0.08	4.4 ± 0.3	9.2 ± 3.2
Benz[*a*]anthracene (BaA)	2.27 ± 0.20	5.3 ± 0.5	12.6 ± 4.5
Benzanthrone (BA)	0.75 ± 0.01	2.3 ± 0.1	3.1 ± 1.1

[a] Given in unit of cm^3 $molecule^{-1}$ sec^{-1}.

[b] $[NO_2]$ and $k_{PAC\text{-}NO3}$ are given in unit of molecules cm^{-3} and cm^3 $molecule^{-1}$ sec^{-1}, respectively.

Table 2: Calculated lifetimes of the compounds studied with respect to gas-phase reaction with OH and NO_3 radicals.

	Lifetime Due to Reaction with	
	OH (h) [a]	NO_3 (day) [b, c]
Chrysene (CHRY)	3.3	36
Benz[*a*]anthracene (BaA)	2.8	27
Benzanthrone (BA)	6.4	108

[a] For a 12-h average daytime OH radical concentration of 1.9×10^6 molecule cm^{-3} [27].

[b] For a 12-h average NO_3 radical concentration of 5×10^8 molecule cm^{-3} [23].

[c] For a 24-h average NO_2 concentration of 6.91×10^{11} molecule cm^{-3} [28].